

## FATE OF ATMOSPHERIC SULFUR AND NITROGEN FROM FOSSIL FUELS

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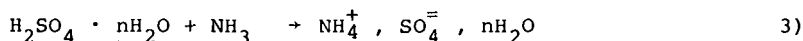
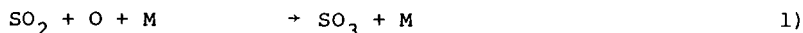
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Sulfur and nitrogen are emitted to the atmosphere during the combustion of coal and other fossil fuels principally as the gases sulfur dioxide ( $\text{SO}_2$ ) and nitric oxide ( $\text{NO}$ ). In uncontrolled systems, approximately 90% of the sulfur in the fuel is converted to  $\text{SO}_2$  and 5% to  $\text{SO}_3$ . The balance is emitted in flyash or collected in the bottom slag. (1) Coal combustion accounts for about 60% of the man-made sulfur oxide emissions (2,3), which represent 1/3 of the total global sulfur emissions to the atmosphere, viz.  $300 \times 10^6$  tons  $\text{SO}_2/\text{yr}$ . (3) Nitrogen oxide emissions during fossil fuel combustion result from high temperature reaction of atmospheric nitrogen and oxygen, as well as partial combustion of nitrogenous compounds in the fuel. Important factors that affect  $\text{NO}$  production include: Flame and furnace temperature, residence time of combustion gases, rate of cooling, and presence of excess air. (1) Coal combustion accounts for 20% of the man-made  $\text{NO}$  emissions, which represent 1/10 of the  $500 \times 10^6$  tons/yr produced by natural sources. (4)

The atmospheric transport, conversion, and fate of sulfur dioxide and nitric oxide is quite complex. While qualitative descriptions of some conversion and deposition mechanisms are available, quantitative estimates of the importance of each mechanism remain crude.

Sulfur dioxide emitted into the atmosphere is advected and dispersed by the general air flow and smaller scale turbulence. Direct adsorption may occur on vegetation and soil surfaces (5).  $\text{SO}_2$  may also be "washed out" in precipitation (6). However, it is generally believed that most  $\text{SO}_2$  is chemically converted to sulfuric acid or a particulate, sulfate before removal from the atmosphere.

In the presence of sunlight,  $\text{SO}_2$  may be oxidized in a three body reaction by photochemically produced monatomic oxygen. (7) Rapid hydration would follow to form a sulfuric acid mist. The presence of ammonia may buffer the reaction and increase production of sulfates. (8)



Other investigators (9, 10, 11) have recently proposed  $\text{SO}_2$  reaction with either  $\text{OH}$  or  $\text{HO}_2$  as an important homogeneous gas-phase conversion mechanism.



This mechanism has been purportedly demonstrated in laboratory experiments (11), but remains to be verified under actual field conditions. The development of a remote monitoring instrument for OH (9) should provide more information on its relative significance.

Direct photo-oxidation of  $\text{SO}_2$  is considered to be negligible. (12)

Heterogenous reactions on solid or liquid surfaces represent a second important class of  $\text{SO}_2$  oxidation mechanism. The presence of heavy metal ions, such as iron or manganese have been observed to catalyze the conversion of  $\text{SO}_2$  to acid sulfates. (13) Oxidation rates are highly dependent on temperature and relative humidity.

Catalytic oxidation may also occur on dry surfaces. Novakor, et al. (14) have demonstrated catalytic formation of sulfate on carbon soot in the laboratory and have identified several sulfur compounds on the surface of carbon particulates collected in urban atmospheres.

Sulfur compounds emitted during combustion and converted to sulfates are ultimately removed from the atmosphere by dry deposition and precipitation. Although the removal rates are not well quantified, the atmospheric residence time is estimated to range between one and seven days. (3) Long range transport of sulfates may therefore extend to hundreds of kilometers from the  $\text{SO}_2$  source. (15, 16, 17,18)

"Ballpark" estimates of net  $\text{SO}_2$  to sulfate conversion rates for several mechanisms are listed below.

Table 1SO<sub>2</sub> to SO<sub>4</sub> Conversion Rates

<u>Mechanism</u>	<u>SO<sub>2</sub> Consumption Rate</u>
Direct photo-oxidation	0.5 %/hr
Indirect photo-oxidation	1-3 %/hr
Air oxidation in liquid droplets	1-20 %/hr
Catalyzed oxidation in liquid droplets	1-20 %/hr
Catalyzed oxidation on dry surface	1-13 %/hr
Observed SO <sub>2</sub> consumption in a coal- fired power plant plume	
70% relative humidity	0.1 %/min
100% relative humidity	0.5 %/min

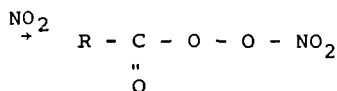
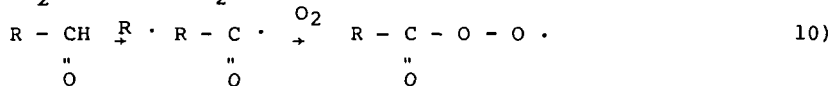
(Table adapted from 19, 20)

Nitrogen compounds are emitted during fossil fuel combustion principally as NO. Oxidation to NO<sub>2</sub> occurs very rapidly, however. Equilibrium values of NO and NO<sub>2</sub> are determined by the following reactions:



The NO/NO+NO<sub>2</sub> ratio is approximately .5 during daylight and .1 at night. (9)

NO may undergo a series of complex chain reactions (typically 100 times slower than the NO + NO<sub>2</sub> reaction) with olefinic hydrocarbons and hydroxyl radicals to form nitrate compounds. A typical sequence might be:



Measurements of nitrate ions in rain (21) suggest that NO<sub>2</sub> is transformed to nitrates in precipitation. However, the direct reaction



has not been shown to be significant in the atmosphere. (4) Two other mechanisms have been suggested recently (9) for nitrous and nitric acid formation during daylight:



Both mechanisms remain to be verified by field measurements of hydroxyls.

Heterogeneous surface catalysis of NO and NH<sub>3</sub> on carbon soot has been proposed by Chang and Novakov (22). In laboratory experiments they have generated volatile ammonium salts at ambient temperatures and reduced nitrogen compounds at elevated temperatures, in qualitative agreement with field observation at urban California sites.

Little information is available on the consumption rate of  $\text{NO}_2$  by the mechanisms described. However, Robinson and Robbins have estimated the residence time of  $\text{NO}_2$  to be three days, based on the total atmospheric nitrogen cycle. (23)

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